

In the United States Patent and Trademark Office

In Re Application of: Yang, et al.	Examiner: Cynthia Hamilton
Serial No.: 09/898,152	Art Unit: 1752
Filing Date: July 3, 2001	Docket No.: 2156-188J
Title: Laser Imaged Printing Plates	

Declaration of Rustom Kanga

I, Rustom Kanga, hereby declare:

1. I have over 13 years of experience in research and development in the area of flexographic printing plate construction, including considerable background in the area of laser imaged printing plates containing a photopolymerizable layer and a laser ablatable layer.
2. I am a co-inventor of the inventions described in the above noted patent application and am employed by the assignee of this application.
3. I received a B.S. (Tech.) degree in 1983 from the University Department of Chemical Technology, Bombay University and a Ph.D degree in 1988 from the University of Florida.
4. I have worked in the area of researching and developing photopolymers and fabrication processes for printing plates for over 13 years. I have also worked with lasers for imaging printing plates and laser-imageable printing plates for over 12 years.
5. I have reviewed, and am an inventor of the inventions described in, the above noted patent application, the parent of which was filed in the U.S.

Patent and Trademark Office on June 25, 1993, a copy of which is appended hereto as Exhibit – pages 1-29. I have also reviewed the claims which are now pending in this present patent application (Serial No. 09/921,589), appended hereto as Exhibit – pages 30-35.

6. I consider myself to be a person having skill in the field to which the pending claims pertain, and also to be a person who had skill in this field at least as early as 1993. In fact, I am an inventor of the claimed subject matter.
7. I understand that the Patent Office has asserted that the currently pending claims contain subject matter that was not described in the June 1993 parent of this patent application in such a way as to reasonably convey the currently claimed subject matter to those skilled in the art.
8. I believe that the subject matter claimed in the pending claims was clearly described in the June 1993 parent of this application. As a person skilled in the art, upon reading the June 1993 parent of this application, it is clear that the subject matter currently claimed was reasonably described in the June 1993 patent application such that the skilled person could reasonably reproduce the invention of the currently pending claims.

This is so for at least the following reasons:

- a. The June 1993 parent of this patent application describes photosensitive elements that comprise a layer that is ablatably by laser radiation and that is placed directly upon a photopolymerizable layer. The June 1993 application does not require that a particular wavelength of laser radiation, or range of wavelengths, be used and, in fact, repeatedly refers to ablation at a “selected wavelength” or at an “appropriate

wavelength” (See, for example, Exhibit - page 8, line 13; Exhibit - page 9, lines 23-24; Exhibit - page 10, line 34 to page 11, line 1; Exhibit - page 12, line 15 and lines 19-20; and Exhibit - page 13, lines 5-6). Consistent with this teaching, the June 1993 patent application indicates, for example, at Exhibit - page 14, lines 15 to 20, that the wavelength of the laser used for ablation must be such that the laser treatment ablates the ablatable layer without extensively damaging the photopolymer to an extent that it cannot subsequently be used as a printing surface.

- b. The June 1993 application contains several examples using UV laser radiation to accomplish this purpose. However, laser wavelengths outside the UV range are also exemplified. For example, Example 3 clearly describes ablation imaging using lasers emitting in the IR range, specifically YAG and CO<sub>2</sub> lasers. This example clearly describes a photosensitive element comprising:

- (1) a photocurable layer (Exhibit - page 18, line 30) – the commercially available KOR photopolymer used in Example 3 comprises 1,6-hexanediol diacrylate and 1,6-hexanediol dimethacrylate as the monomers;
- (2) an infrared ablatable layer in direct contact with the photopolymerizable layer (Exhibit - page 15, lines 1-9 and Exhibit - page 18, line 31, through page 19, line 2) comprising:
  - (a) a UV absorbing material (Exhibit - page 15, line 9);
  - (b) a binder (i.e. Macromelt® 6900, a polyamide) (Exhibit - page 15, line 8);

wherein the infrared ablatable layer is exposed to and ablated by an infrared laser (i.e. a CO<sub>2</sub> laser).

Example 3 concludes with the following sentence:

**“Thus, it was seen that the basic idea of the laser-imaged printing plate was demonstrated...”**

In addition Table II (1993 patent application, Exhibit - page 20) clearly reports successful results. Although runs 2, 5 and 6 in Table II report that not enough ablation was achieved, the result achieved was workable and could easily be optimized by adjusting the power of the laser. Further runs 8 and 12 reported full ablation and, particularly run 12, a completely workable result. The issue of unevenness of the plate surface is again the subject of mere slight modification to the laser power.

In fact as an inventor I have carried out these minor modifications to the laser power and produced excellent results as later discussed herein and as described in the Exhibit – pages 36-44. Further, with minor modifications to the power of the laser, excellent results were also achieved as noted in the above-described Exhibits.

c. Claims 1-15, which were originally filed with the June 1993 application, were not limited to lasers operating at a particular wavelength or range of wavelengths but instead to the use of a laser at a selected wavelength.

9. The June 1993 patent application also clearly indicates that the ablatable layer comprises a UV absorbing material. This UV absorbing material

allows the ablatable layer to act as a mask to the UV flood lamps that are used, after ablation occurs, to polymerize the desired portions of the photopolymerizable layer. In the examples of the June 1993 patent application the preferred UV absorber is Uvinul<sup>TM</sup>. Uvinul<sup>TM</sup> is in fact also an IR absorber, as most materials are. The UV absorber is mixed with a binder, in this case a polyamide (Macromelt® 6900) (see Exhibit - page 11, lines 2-5), to form the infrared ablatable layer.

10. As a person skilled in the art to which this invention pertains, I know that most materials are both UV and infrared absorbers. I also know that the UV absorbers described in my invention, including Uvinul<sup>TM</sup>, are both UV and infrared absorbers.
11. The June 1993 patent application states that “UV flood lamps normally provide the light for curing” (Exhibit - page 11, lines 26-27), and indicates that the presence of a UV absorber in the ablatable layer imparts UV opacity to the layer (Exhibit - page 9, lines 31-33). The June 1993 patent application further states that the spectral range of the flood-exposure lamps used “in most applications” is 300-400 nm, that the UV absorber “typically should be active in this range”, and that an alternative way of stating this is to say that the UV absorber must have a high extinction coefficient “in the spectral output range of the developer lamps” (Exhibit - page 10, lines 5-11). A UV absorber as described in the specification of the June 1993 patent application, is a material that absorbs the radiation used during the curing process, giving the ablation layer opacity to such radiation. A person skilled in the art would know that the UV absorber may also absorb IR radiation, as almost all materials do. Such is the case with all of the UV absorbers described in the June 1993 application (Exhibit - page 10, lines 16-33) (i.e., the materials absorb both UV and IR radiation). This would be apparent to any person skilled in the art.

12. Claim 15 is one of the independent claims pending in the instant application. This claim is clearly supported by the June 1993 parent application as follows:

A process for making a photosensitive element comprising the steps of:

- providing a photosensitive element                      Exhibit - page 3, lines 3-18.  
comprising:
  - a) a backing layer                      Exhibit - page 3, lines 7-9.
  - b) at least one layer of a photo-                      Exhibit - page 3, lines 9-13 .  
curable composition  
on the backing layer
  - c) ablation layer comprising                      Exhibit - page 11, lines 2-5  
and 18-24.
    - i) ultraviolet radiation absorb-                      Exhibit - page 11, lines 6-16.  
ing material
    - ii) at least one binder which is                      Exhibit - page 11, line 29  
selected from the                      through page 12, line 3.  
group consisting of polyacetals,  
polyacrylics, polyamides,  
polyimides, polybutylenes,  
polycarbonates, polyesters,  
polyethylenes, polyphenylene  
ethers, and polyethylene  
oxides;  
slip film in direct contact with                      Exhibit - page 15 , lines 1-22.  
photocurable layer
    - slip film ablatable from the surface                      Exhibit - page 14, lines 15-20.  
of the photocurable layer

upon exposure to infrared laser  
radiation;

- ablating said ablation layer using a laser,      Exhibit - page 14, lines 15-20.  
thereby providing ablated and  
unablated areas forming an image; and
- flood exposing said ablated element to      Exhibit - page 14, lines 15-20  
UV light without a negative, thereby curing  
said photocurable layer in areas under  
ablated areas of said ablation layer.

Specific support for the other claim elements has been previously noted herein. In addition, independent claim 46 contains many of the same features as claim 15 and would also be fully supported by the June 1993 parent application. As can be seen from the June 1993 parent application, the invention described therein clearly comprises doping a slip film layer with a UV absorber and then ablating the layer with a laser at a selected power and wavelength to create an in situ mask (see Exhibit - page 14, lines 15-20). The ablation layer is clearly disclosed as comprising a binder selected from the group consisting of polyacetals, polyacrylics, polyamides, polyimides, polybutylenes, polycarbonates, polyesters, polyethylenes, polyphenylene ethers, and polyethylene oxides (see Exhibit - page 11, line 29 through page 12, line 3). Clearly each and every element of pending claim 15 (and its dependent claims) is supported and enabled by the specification.

13. I further understand that the Patent Office has rejected the currently pending claims of this application under 35 U.S.C §102(e) and/or 35 U.S.C. §103(a) in view of U.S. Patent No. 6,238,837 (the '837 Patent). This rejection is not correct since I had possession of the invention claimed in the currently pending claims far before the filing date of the '837 Patent

as described in the Exhibit – pages 36-44. Each of Exhibit pages 36-44 is dated prior to the June 1993 filing date of this application, but the dates have been redacted in order to maintain the secrecy of the date of my invention. Exhibit pages 36-44 clearly show full completion of the invention described in the currently pending claims prior to the June 1993 filing date of this patent application as noted below:

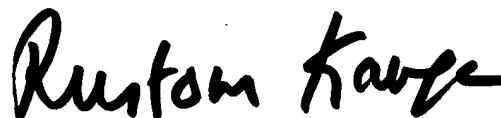
- a) Exhibit – pages 36-37, dated before the June 1993 effective filing date of this application, discusses the doping of a slip layer with a UV absorber (i.e., mixing the absorber with a binder) to create a laser ablatable layer to directly image a printing plate.
- b) Exhibit – page 38, dated before the June 1993 effective filing date of this application, discusses various possible laser ablatable layers, including a layer comprising carbon black as the UV absorber. (A person skilled in the art at the time the invention was made would know that carbon black is usable as an IR absorber.)
- c) Exhibit – page 39, dated before the June 1993 effective filing date of this application, discusses a successful YAG laser ablation of a laser ablatable layer on a photopolymerizable layer.
- d) Exhibit – page 40, dated before the June 1993 effective filing date of this application, discusses successful ablation of an IR ablatable layer on a photopolymerizable layer (EPIC) using YAG and CO<sub>2</sub> lasers. **Further the obvious effects of variations in laser power are discussed.**
- e) Exhibit – pages 41-44, dated prior to the June 1993 effective filing date of this application, clearly reveals the successful ablation of an IR ablatable layer with a CO<sub>2</sub> laser emitting in the IR range. The IR



ablatable layer comprises a UV absorber (Uvinul<sup>TM</sup> D-50) and an IR absorber (Uvinul D-50) in a polyamide binder (Macromelt® 6900). The IR ablatable layer is placed directly on the photopolymerizable layer (Flexlight KOR). The Exhibit concludes with the following:

“The ablated KOR plate can be imaged in UV exposure unit without using a negative and get a great image quality plate”  
(Exhibit – page 43).

14. Thus the invention currently claimed in the pending application was clearly and effectively disclosed in the specification and claims filed on June 25, 1993 and was clearly in my possession prior to June 25, 1993.
15. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful statements may jeopardize the validity of this application or any patent issuing thereon.



Rustom Kanga

Date:

7/21/2004

Ref. 01-8480

**LASER IMAGED PRINTING PLATE**

Inventors: Michael W. Yang  
Ruston S. Kanga  
Alvin V. Randall

### Field of the Invention

5 This invention relates to printing plates which can be made without using a negative. More specifically, it relates to a laser-imageable printing plate. Such plates are particularly useful for flexographic printing, but can be used for offset and lithographic printing.

### Background of the Invention

10 Flexography is a method of printing that is commonly used for high-volume runs. Flexography is employed for printing on a variety of substrates such as paper, paperboard stock, corrugated board, films, foils and laminates. Newspapers and grocery bags are prominent examples. Coarse surfaces and stretch films  
15 can be economically printed only by means of flexography. Flexographic printing plates are relief plates with image elements raised above open areas. One type of flexographic printing plate resembles a transparent or translucent plastic doormat when it is  
20 ready for use. The plate is somewhat soft, and flexible enough to wrap around a printing cylinder, and durable enough to print over a million copies.

Such plates offer a number of advantages to the printer, based chiefly on their durability and the ease with which they can be made. Further  
25 improvements, to the degree of resolution (fineness of detail) which can be obtained as well as reductions in cost, would expand the usefulness of these plates. The present invention allows both increased resolution  
30 by use of laser processing, and reductions in cost

through the elimination of the use of a negative to make the printing plate.

5 A typical flexographic printing plate as delivered by its manufacturer is a multilayered article made of a backing, an unexposed photocurable layer, a protective layer or slip film, and a cover sheet. The backing lends support to the plate. It is typically a plastic sheet about 5 mils or so thick, which may be transparent or opaque. The photocurable layer may be anywhere from about 25-275 mils thick, and can be formulated from any of a wide variety of known photopolymers, initiators, reactive diluents, fillers, etc. The slip film is a thin (about 0.1 - 1.0 mils) sheet which is transparent to UV light that protects the photopolymer from dust and increases its ease of handling. The cover sheet is a heavy, protective layer, typically polyester, plastic or paper.

20 In normal use, the printer will peel the cover sheet off the printing plate, and place a negative on top of the slip film. The plate and negative will then be subjected to flood-exposure by UV light through the negative. The areas exposed to the light cure, or harden, and the unexposed areas are removed (developed). Typical methods of development include washing with various solvents or water, often with a brush. Other possibilities for development include use of an air knife or heat plus a blotter.

30 Exposure of the printing plate is usually carried out by application of a vacuum to ensure good contact between the negative and the plate. Any air gap will cause deterioration of the image. Similarly, any foreign material, such as dirt and dust between the

negative and the plate results in loss of image quality.

5 Even though the slip films are thin and made from transparent materials, they still cause some light scattering and do somewhat limit the resolution which can be obtained from a given image. If the slip film were eliminated, finer and more intricate images could be obtained.

10 Finer resolution would be particularly desirable for the reproduction of elaborate writing as in the case of Japanese characters, and for photographic images.

15 A negative can be a costly expense item. For one thing, any negative which is used for printing must be perfect. Any minor flaw will be carried through onto each printed item. As a consequence, effort must be expended to ensure that the negative is precisely made. In addition, the negative is usually made with silver halide compounds which are costly and which are also the source of environmental concerns upon disposal.

20 Given these considerations, it is clear that any process which would eliminate the use of the negative, or reduce the light scattering effects and other exposure limitations of the slip films, would yield significant advantages in terms of cost, environmental impact, convenience, and image quality over the present methods.

25 The inventors have found a way to obtain these advantages by using a laser guided by an image stored in an electronic data file to create an *in situ* negative on a modified slip film, and then exposing and developing the printing plate in the usual manner. As a result, the printer need not rely on the use of

- 5 -

negatives and all their supporting equipment, and can  
rely instead on a scanned and stored image. Such  
images can be readily altered for different purposes,  
thus adding to the printer's convenience and  
flexibility. In addition, this method is compatible  
with the current developing and printing equipment, so  
expensive alterations to the other equipment are not  
required.

Laser engraving of various materials, such as  
wood and metal, is well known. Laser engraving of  
cured hard rubber or lithographic plates is also  
known. If this procedure were applied to a  
flexographic printing plate, the plate would first be  
exposed to UV light without an image. Then the laser  
would be used to engrave an image on the hardened  
plate. This has been attempted, but found to be too  
slow to be commercially competitive. Flexographic  
printing plates require a high relief (30-40 mil high  
letters) which take a long time to engrave.

Direct exposure of a photopolymer using a laser  
is also known. This procedure use a precisely guided  
laser to replace the UV flood lamps which are normally  
used to expose the plate. United States Patent  
4,248,959, issued to Jeffers et al. February 3, 1981,  
relates to the direct exposure of a photosensitive  
polymer plate using a laser guided by a computer-  
generated image. The disclosed method is not suitable  
for the development of flexographic printing plates,  
again because the thickness of the plate hampers the  
cure. Again, the process is too slow to be  
commercially competitive.

Other efforts have focussed on generating an  
image directly in contact with a photocurable layer.  
United States Patent 5,015,553 issued to Grandmont et

al. May 14, 1991 relates to a method of making a UV photoresist for a printed circuit board, using a computer-assisted design (CAD) driven photoplotter which selectively exposes a photographic imaging layer without affecting the underlying UV sensitive photoresist. The image layer is then chemically developed on the board and used as an situ mask for the underlying UV resist during exposure to UV light. After the exposure, the image layer is peeled off to allow conventional processing of the resist. The process requires at least two development steps for the entire plate, and also requires the use of a peelable cover sheet interposed between the image layer and the photocurable layer.

Laser ablation of polymers from relatively insensitive substrates is known. United States Patent 4,020,762 issued to Peterson May 3, 1977 relates to a method of making a sensitized aluminum printing plate for offset lithography. An aluminum sheet was coated with a mixture of finely divided carbon, nitrocellulose, a non-oxidizing alkyd resin, a diazo sensitizer, cellulose acetate, butylacetate, xylene and ethyl cellosolve. The coating was at least partially etched with a YAG laser. It is not clear whether all the coating was removed from the aluminum substrate although the text alludes to this result. The patentee discloses that the etched areas became sensitive to UV light, and that the etched areas, after exposure to UV light and development, accepted ink, while the areas which were not etched accepted water. No quantitative results are presented. There is no indication that the liquid coating in the reference would be usable as a flexographic printing plate. There is no indication that the laser ablation

was precise enough to allow removal of a polymer layer to uncover a photosensitive polymer layer directly beneath.

5 Lasers have also been used to physically transfer small amounts of polymer from one layer of a multilayer article to another. United States Patent 5,156,938 issued to Foley et al. October 30, 1992, relates to a method of laser-induced ablative transfer imaging suitable for the production of masks  
10 (negatives) for the graphic arts and printed circuit industries. In this process, a laser-sensitive material is physically displaced from a donor layer of a multilayer structure to a receptor layer.

15 This is described as an ablative transfer because some of the materials from the donor layer are ablated while other materials are deposited on the receptor layer.

20 The inventors have discovered that if a slip film, of the type already in use with flexographic plates, is modified with a strong UV absorber, a laser can be used to engrave the slip film instead of the photopolymer. The slip film, then, effectively becomes a negative that is created in situ. There is  
25 no need to separately manufacture a negative, or to eventually dispose of silver halide. Also, the light scattering effects of the slip film are eliminated, thereby increasing resolution of the image.

#### Objects of the Invention

30 It is therefore an object of the present invention to provide a method of making a printing plate which does not require the use of a photographic negative.



Another object of this invention is to make a laser-imageable printing plate.

Yet another object of this invention is to provide a protective layer for a photocurable article that can be conveniently and accurately removed by laser ablation from the article.

The objects of this invention can be accomplished by providing a protective layer for a photocurable article comprising

- a polymeric matrix and
- a dopant having a high extinction coefficient in the range of 300-400 nm, the layer responding to a threshold dosage of radiation at a selected wavelength by photoablation of the polymeric matrix and, preferably, photobleaching of the dopant. The layer is applied to a photosensitive article, and then a laser is employed to selectively remove the protective layer, exposing the photocurable composition underneath to subsequent exposure to UV light and cure. The cured plate then can be developed in the normal fashion.

Other objects and advantages of this invention will become apparent through the disclosure herein.

### Detailed Description of the Invention

#### The Exposure and Development Process

The present invention includes a method of making a laser imaged printing plate. First, a solid, uncured printing plate is modified with a UV absorber. This is most conveniently done by adding a UV absorber to the normally UV transparent slip film which is already adapted for use with the printing plate, and applying the same in the usual fashion to the surface

of the uncured printing plate. The printing plate with the modified slip film can be stored for a time, or used immediately, as the printer's needs dictate.

When the printing plate is to be used, a laser is employed to selectively ablate, or remove, the slip film. The uncured plate is then flood-exposed to UV light in the usual fashion. The areas where the slip film was ablated will cure, or harden, upon exposure to the UV light. The areas where the slip film was not ablated will remain uncured. The uncured areas can then be washed away in the normal development process.

This application is written in terms of the specific embodiment in which the invention was first applied, that is, flexographic printing plates. One of ordinary skill in the art will readily recognize that this invention is not limited to this embodiment. For example, in this invention the slip film is used as a carrier for the UV absorber. This is a matter of convenience, as the slip film was already available in the existing plates for use. Similarly, a UV transparent film which has been doped with a UV absorber and ablated by a laser operating at a selected wavelength could be used as the printing sleeve for gravure printing, or as an in situ mask for making photoresists.

#### The UV Absorber

One important aspect of the present invention is that the slip film, which would normally be transparent to UV light in order to facilitate the imaging process, is modified with a UV absorber. The presence of the UV absorber makes a normally UV transparent slip film into highly UV opaque barrier.

It is critical that the UV absorption be nearly complete, at least 97%, preferably more than 99.9%, and even more preferably 99.99%, so that substantially all the radiation from the UV flood-exposure lamps will be blocked. The spectral range of the flood-exposure lamps used in most applications is 300-400 nm. Therefore the UV absorber typically should be active in this range. An alternative way of stating this is to say that the UV absorber must have a high extinction coefficient in the spectral output range of the developer lamps.

Benzophenone derivatives and strongly absorbing dyes are favored. The following materials have high extinction coefficients within the typical spectral range of developer lamps:

Uvinul D 49™ (2,2'-dihydroxy-4,4'-dimethoxybenzophenone) available from BASF Corp., Parsipanny, NJ;

Uvinul D 50™ (2,2',4,4'-tetrahydroxybenzophenone) available from BASF Corp., Parsipanny, NJ;

Uvinul N 539 (benzophenone cyanoacrylate) available from BASF Corp., Parsipanny, NJ;

4-(dimethylaminobenzophenone) available from Aldrich Chemical Company, Milwaukee, WI;

Tinuvin P™ (benzotriazole) available from Ciba-Geigy Corp., Hawthorne, NY;

Intrawite OB™ A dye Available from Crompton & Knowles Ltd, Reading, PA;

Intraplast Yellow 2GLN, a dye available from Crompton & Knowles;

4-phenylazophenol ("4-PAP") available from Aldrich.

The UV absorber must also exhibit a specific response to excitation by laser at an appropriate

wavelength: It must allow the ablation of the slip film. Finally, the UV absorber must be compatible with the slip film, and not exhibit significant migration from the slip film to the photocurable composition.

Preferred UV-absorbers which have been found to have these characteristics are Uvinul<sup>®</sup> D 49 and D 50 (BASF) and 4-phenylazophenol. These materials cause photoablation of a typical slip film upon exposure to a threshold power level (fluence) at the selected wavelength of 351 nm. In addition, they have the added advantage of photobleaching at 351 nm. The UV absorber is typically present in the film in amounts of about 1-20 PHR (parts per hundred, or 1/101-20/120 percent); preferably about 4-8 PHR when the slip film is 0.1 to 1.0 mils, preferably 0.3 to 0.5 mils.

#### The Slip Film

As discussed above, the preferred vehicle for the UV absorber in some embodiments of the present invention is the slip film, a thin, protective film used with a printing plate which is to be imaged. These films are made of a wide variety of polymers which are compatible with the underlying photopolymer and easily removed during the development (wash) step. When a negative is used, the slip film has to be transparent to the light used for curing. Since UV flood lamps normally provide the light for curing, the normal slip film is transparent in the range of 300-400 nm. Such films are well known in the photoprocessing field, and in principle, any such film may be modified by adding the UV absorber of the present invention. Examples include polyacetals, polyacrylics, polyamides, polyimides, polybutylenes,

polycarbonates, polyesters, polyethylenes, cellulosic polymers, polyphenylene ethers, and polyethylene oxides. Cellulosics and polyamides are preferred. The addition of the UV absorber may change the film's response to the laser used in the present invention. For example, many films are not normally affected by exposure to laser radiation at 351 nm, but when Uvinul D 50 is added, these films become vulnerable to laser ablation, and useful in the present process.

#### The Photocurable Composition

In principle, any of the known photocurable formulations can be used in the present invention. However, it is particularly helpful if the type of photopolymer and initiator used are compatible with the laser or the wavelength selected for use in the process.

#### Photopolymer

Of the photopolymers, those which are unaffected by laser radiation at the particular wavelength selected for the practice of the present invention are particularly useful. Of these, polyurethanes, including acrylate polyurethanes, acid-modified acrylate polyurethanes, amine-modified polyurethanes, rubbers, including acrylonitrile rubbers, and [di- and triblock copolymers such as those made from styrene-isoprene and styrene-butadiene may be mentioned. [The amine-modified acrylate polyurethanes and styrene-isoprene or styrene-butadiene di- and triblock copolymers are preferred.] An uncured printing plate made from such a photopolymer can withstand some exposure to the laser energy without incurring thermal damage. Thus the photopolymer and various additives

except the initiator should have a low absorbance at the laser's operating wavelength.

### Initiator

5       The initiator can also have a low absorbance at the wavelength of the laser selected for use in the present invention. However, if the initiator is activated in response to the selected wavelength, cure of the photopolymer will begin during the ablation step, without damage to the photopolymer, before  
10       flood-exposure by the UV lamps. Use of the appropriate initiator can, therefore, speed processing of the plate and help insure a faster, more uniform cure.

15       Photoinitiators for the photocurable composition include the benzoin alkyl ethers, such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether and benzoin isobutyl ether. Another class of photoinitiators are the dialkoxyacetophenones exemplified by 2,2-dimethoxy-2-phenylacetophenone,  
20       i.e., Irgacure® 651 (available from Ciba-Geigy, Hawthorne, NY); and 2,2-diethoxy-2-phenylacetophenone. Still another class of photoinitiators are the aldehyde and ketone carbonyl compounds having at least one aromatic nucleus attached directly to the carboxyl  
25       group. These photoinitiators include, but are not limited to, benzophenone, acetophenone, o-methoxybenzophenone, acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone, alpha-phenyl-  
30       butyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, 4'-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4'-methoxyacetophenone, benzaldehyde, alpha-tetralone, 9-acetylphenanthrene,

2-acetylphenanthrene, 10-thioxanthenone, 3-acetylphenanthrene, 3-acetyllindone, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one, 7-H-benz[de]-anthracene-7-one, 1-naphthaldehyde, 4,4'-bis(dimethylamino)-benzophenone, fluorene-9-one, 1'-acetonaphthone, 2'-acetonaphthone, 2,3-butanedione, acetonaphthene, benz[a]anthracene 7.12 dione, etc. Phosphines such as triphenylphosphine and tri-o-tolylphosphine are also operable herein as photoinitiators.

Benzophenone-based initiators are preferred. An example that is commercially available is Irgacure 651.

#### The Laser

A laser is employed to precisely remove the slip film exposing the photopolymer underneath to subsequent flood exposure and cure. The wavelength and power of the laser should be such that the laser treatment can ablate the slip film without damage to the photopolymer layer just beneath. Excimer lasers which operate in a pulse mode having a wavelength of  $350 \pm 50$  nm, preferably about 351 nm are usable. The preferred dosage level is 1-5 Joules per  $\text{cm}^2$  ( $\text{J}/\text{cm}^2$ ).

The following examples illustrate the present invention without limiting it, or the claims which follow.

#### Example 1

##### Preparation of Uvinul D 50 Modified Polyamide Slip Film For KOR Flexographic Plates

In this example, the slip film which would normally be used with a commercially available flexographic printing plate is modified by the addition of a UV absorber so that zero transmittance

(as demonstrated by protection from cure upon exposure to UV flood lamps) is achieved.

A stock casting solution was prepared with the following formulation:

Isopropanol	45.6 parts
Hexane	23.9 parts
VM&P Naphtha <sup>1</sup>	21.6 parts
Macromelt 6900 <sup>M2</sup>	8.3 parts
Uvinul D 50	0.664 parts

Footnote:

- <sup>1</sup> Aromatic solvent mixture available from Ashland Chemical Co., Columbus, OH
- <sup>2</sup> Polymer pellets available from Henkel Corp., Lagrange, IL

Films approximately 5 to 7 mils thick were hand cast on a clear Mylar<sup>TM</sup> backing sheet using a drawdown bar. Upon drying, the average film thickness was measured using a Ono Sokki micrometer to be around 0.3-0.5 mils.

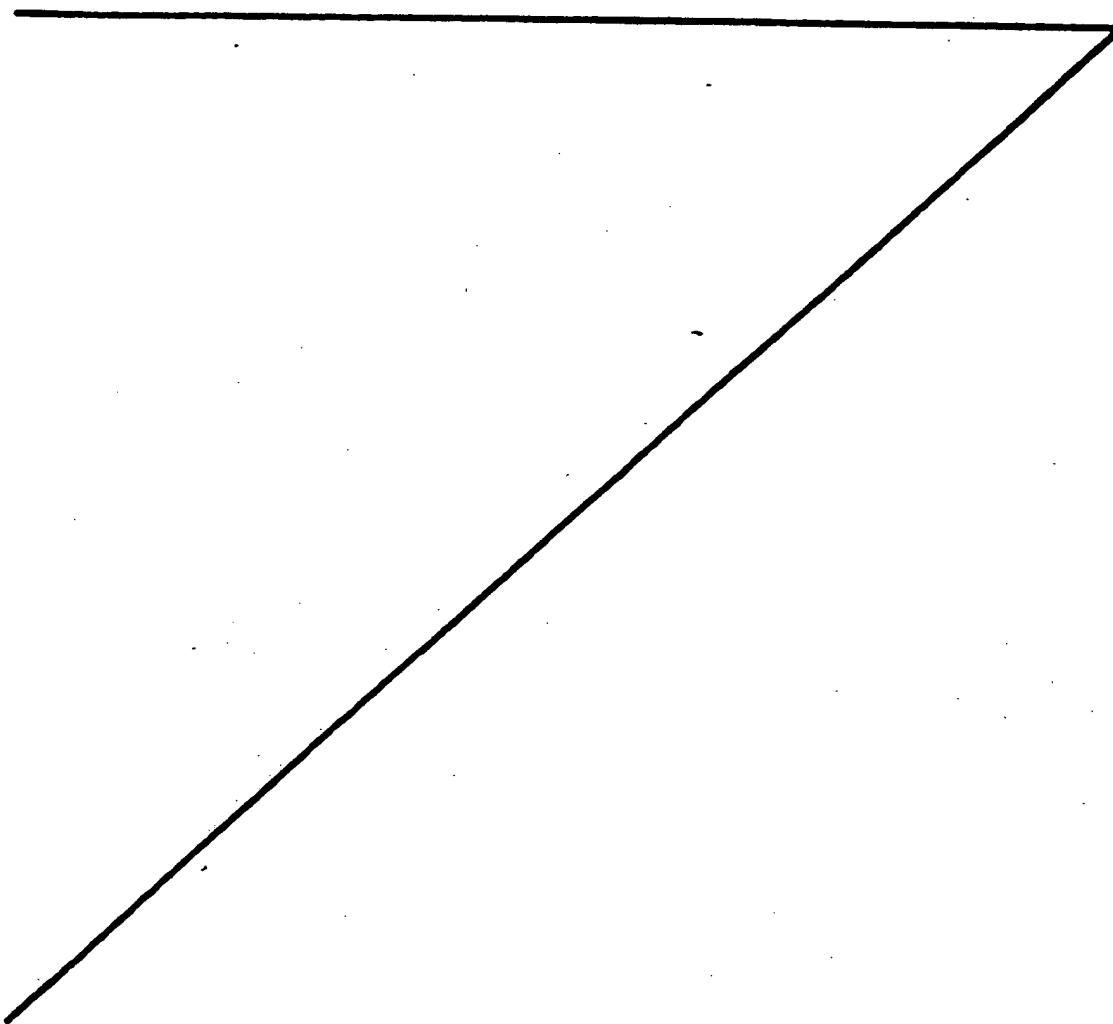
The films were laminated onto a commercially available photopolymer composition to make a UV absorber-modified printing plate analagous to the KOR<sup>®</sup> printing plate available from W. R. Grace & Co.-Conn., Atlanta, Ga. The plates were exposed through a test negative using commercially available UV flood lamps. Three different concentrations (4 PHR, 6 PHR and 8 PHR based on percent solids), three levels of thicknesses (low, medium and high) and two exposure levels were employed for the study which is summarized in Table I. Presence or absence of an image was an indication of the effectiveness of the UV absorber for blocking the incident UV radiation. For the 4 and 6 PHR loadings, an image was seen when the slip thickness was less than 0.4 mils, indicating a lower threshold concentration of D 50 to effectively block all UV light. For 8 PHR loadings, 0.3-0.4 mils was seen to



be sufficient to block all UV light as seen by an absence of an image. For all three concentrations, a thickness above 0.5-0.6 mils was effective.

5

The modified slip film was then laminated onto a Flex Light KOR® ("KOR") plate which was approximately 25 to 275 mils thick. The laminated plates were annealed at 75° F, and used for laser ablation trials, as shown in Examples 3-6.



**TABLE I**  
**Studies on the Concentration of Uvinul D 50**  
**Versus Thickness of the Slip Film**

Concentration <sup>1</sup>	Thickness		Exposure	
	Wet (mils)	Dry (mils)	3½ min.	7 min.
4 PHR	7	0.1-0.2	I <sup>2</sup>	I
4 PHR	10	0.2-0.3	I	I
4 PHR	15	1.4-1.5	N <sup>3</sup>	N
6 PHR	7	0.2-0.3	I	I
6 PHR	10	0.4-0.5	N	N
6 PHR	15	0.7-0.8	N	N
8 PHR	7	0.3-0.4	N	N
8 PHR	10	0.4-0.5	N	N

## Footnotes:

- 1 - Per hundred based on percent solids.  
 2 - I: Formation of image. D 50 not effective in blocking UV light.  
 3 - N: No image. D 50 effective.

**Example 2**

**Preparation of Uvinul D 50 Modified Cellulosic-Based  
Water-Wash Slip Film for Amine-Modified Polyurethane  
(AMPU) Aqueous-Developable Flexographic Plates**

5           In this Example, another type of slip film, a  
cellulose film adapted for use with a water-washable  
flexographic printing plate, is modified with a UV  
absorber. The concentration and thickness found in  
10           the previous Example were utilized to ensure the  
maximum UV absorption by the film.

A stock solution was prepared using the following  
formulation:

Isopropanol	50.2 parts
Water	39.8 parts
15       Klucel L <sup>1</sup>	10.0 parts
Uvinul D 50	0.8 parts

**Footnote:**

- 20           <sup>1</sup>       Hydroxypropyl cellulose polymer pellets available  
from Aqualon, Inc., Wilmington, DE

25           As before, films 5 to 7 mils thick were cast on a  
clear Mylar™ backing sheet, dried and laminated onto a  
developmental amine-modified polyurethane flexo  
substrate. The plates were between 25 mils and 275  
mils thick. Laser ablation and imaging was carried  
out on the modified plates as shown in Examples 3-6.

**Example 3**

**Laser Ablation and Imaging Using a  
Solid-State Sealed CO<sub>2</sub> Laser (10.6 nm)**

30           The commercially available photopolymer resin of  
Example 1 was formed into a sheet and laminated with  
0.9 mil thick polyamide slip film containing 8 PHR

Uvinul D 50 to make an experimental printing plate (KOR). The plates for this preliminary study were prepared using a hand cast slip film. Two different laser systems were employed for the ablative studies: a sealed-CO<sub>2</sub> absorbing at 10.6  $\mu$ m and a YAG at 1.06  $\mu$ m. The YAG laser was found to be essentially ineffective in causing any ablation. The power in the sealed-CO<sub>2</sub> laser was varied from 8 watts to a high of 15 watts. Digital image programming allowed ablation of a rectangular profile (1 cm x 2 cm) and also lettering. Results from the ablative studies are summarized in Table II.

The presence or absence of the polyamide slip film was investigated by ATR-IR analysis. The ablated plate was then flood exposed with hot lamps for 6 minutes and developed in Solvit®, the usual development solvent for commercial purposes available from Polyfibron Division of W. R. Grace & Co.-Conn., Atlanta, GA, for 6 minutes. From Table II it is seen that the etch depth versus fluence (power) was not linear. The difference in etch depth between 8 to 10 Watts is barely more than the experimental error of 0.1 mils. At 12 Watts, the 0.5 mil slip film had been complete ablated, along with some of the underlying photopolymer. There was also a jump in the etch depth from 0.7 mils to 5.0 mils when the power is increased from 12 watts to 15 watts. As expected, only those rectangular profiles which show almost complete ablation of the slip film cured during subsequent flood exposure and development. However, even for those profiles, the surface was highly textured and

**TABLE II**

**CO<sub>2</sub> Laser-Ablative Imaging Studies on Uvinul D 50  
Modified Slip Film Laminated on KOR**

#	Power Watts	Etch Depth mils	Plate Imaging		Comments
			Rectangular Profile	Lettering	
2	8	-	Washed away	Washed away	Not enough ablation
5	9	0.1-0.3	Washed away	Washed away	Not enough ablation
6	10	0.3-0.4	Washed away	Washed away	Not enough ablation
8	12	0.7	Cured, 68 mils	Washed away	Plate surface uneven
12	15	5.0	Cured, 64 mils	Cured	Plate surface uneven

rough. Also, the resolution was poor for the letters. Thus, it was seen that the basic idea of the laser-imaged printing plate was demonstrated, and that use of the CO<sub>2</sub> laser resulted in thermal ablation with a consequent loss of resolution.

Example 4

Laser ablation and imaging using Krypton Fluoride (KrF) Excimer Laser at 248 nm

The experimental printing plates made according to Example 1 (KOR) and 2 (AMPU) above were imaged as in Example 3 using a krypton fluoride excimer laser controlled by digital imaging programming. The results are summarized in Table III.

The krypton fluoride excimer laser at 248 nm was found to be extremely effective in causing photoablation. Since most polymers including the polyamide of the slip film and the Kraton™ rubber of the photopolymer of Example 1 have very strong absorption at 248 nm, even small fluences (<0.5 J/cm<sup>2</sup>) caused ablation of the slip. The mechanism is believed to be mainly photoablation (i.e., chemical bond-breaking of the polyamide) and some thermal ablation due to heat generation. Unfortunately, since the styrene-isoprene rubber used to make the photopolymer is also very strongly absorbing at this wavelength, some damage to the surface occurred, especially at higher fluences. Where thermal damage occurred, resolution was poor.

**TABLE III**

**Laser Ablation of KOR and AMPU Using  
KrF Excimer Laser (248 nm)**

Type	Fluence J/cm <sup>2</sup>	# of Pulses	Image	Comments
KOR (Ex.1)	0.4	10	Yes	Thermal Damage. Poor resolution for all.
		40	Yes	
		70	Yes	
	1.2	1	No	Swell due to incomplete cure. Poor resolution.
		2	No	
		6	Yes	
		8	Yes	
AMPU (Ex.2)	0.4	10	Yes	Thermal Damage. Poor resolution
		40	Yes	
		20	Yes	
	1.2	1	No	Incomplete Ablation
		2	No	
		6	Yes-	Thermal Damage. Poor resolution
		8	Yes	

Example 5

Optimisation of Fluences for  
351 nm Xenon Fluoride (XeF) Excimer Laser

5 Laser ablation and imaging studies and optimization of  
fluences necessary for ablation was carried out as before  
on KOR (Ex. 1) and AMPU (Ex. 2). Similar results were seen  
for both types of plates. The consolidated results are  
summarized in Table IV.

10 Most polymers do not absorb at 351 nm. However, the  
modified slip films (both the solvent-based polyamide and  
the aqueous-based cellulosic polymers) were very sensitive  
to the excimer laser at 351 nm due to the high extinction  
coefficient of D 50 at this wavelength. A combination of  
15 photobleaching (destruction of D 50 molecules) and  
photoablative (transfer of the energy absorbed by D 50 to  
the polymer causing bond breaking in the polymer) effects  
were seen.

20 The modified slip is partially ablated at lower doses  
( $<1 \text{ J/cm}^2$ ) resulting in either no cure (and hence no image)  
or incomplete cure (and hence poor image and resolution).  
A complete ablation was seen at higher doses ( $>1.5 \text{ J/cm}^2$ ).  
There was no damage to the plate surface. Subsequent flood  
exposure and development gave a very sharp image of the  
ablated area with good resolution.



TABLE IV

**Optimization of Fluences for Laser Imaging Using  
Xenon-Fluoride Excimer Laser at 351 nm  
for KOR and AMPU**

Fluence J/cm <sup>2</sup>	# of Pulses	Image	Comments
0.14	50	No	Fluence was below the threshold and hence incomplete ablation
	100	No	
	200	No	
0.4	5	No	Below threshold fluence. Did not cure.
	10	No	
	15	No	
	30	No	
0.9	1	No	Not enough ablation. Not enough ablation. Incomplete cure, image swelled in solvent. Poor resolution.
	2	No	
	6	Yes	
	10	Yes	
1.6	1	No	Not enough ablation. Good resolution, good image. No damage seen to the surface.
	3	Yes	
	5	Yes	

Example 6

**Imaging Studies on KOR Laminated with D 50 Modified  
Slip and Print Test with the Imaged Plate**

Imaging of D 50 modified slip on KOR was carried out using a xenon fluoride excimer laser lasing at 351 nm.

Imaging of lettering was achieved using a CAD file. The following intensities and number of pulses were utilized:

Fluence J/cm <sup>2</sup>	# of Pulses
1.5	8
2.0	6
3.1	4

The ablated/imaged plates were flood exposed under hot lamps for 5 1/2 minutes and washed in Solvit® for 6 minutes to give an image with 20-25 mils relief.

Microscopic examination confirmed that the image quality for all fluences was good, giving sharp profiles. However, the edges were rounded due to insufficient doses in those areas. There was no indication of surface thermal damage and the plate surface was smooth and even in all cases.

#### Example 7

#### Laser Ablation and Imaging on a Slip Modified with 4PHR D 50 and 4PHR 4-phenylazophenol (4-PAP)

In this Example, a mixture of UV absorbers was used with a slip film similar to that of Example 1. A casting solution for the modified slip was prepared using the following formulation:

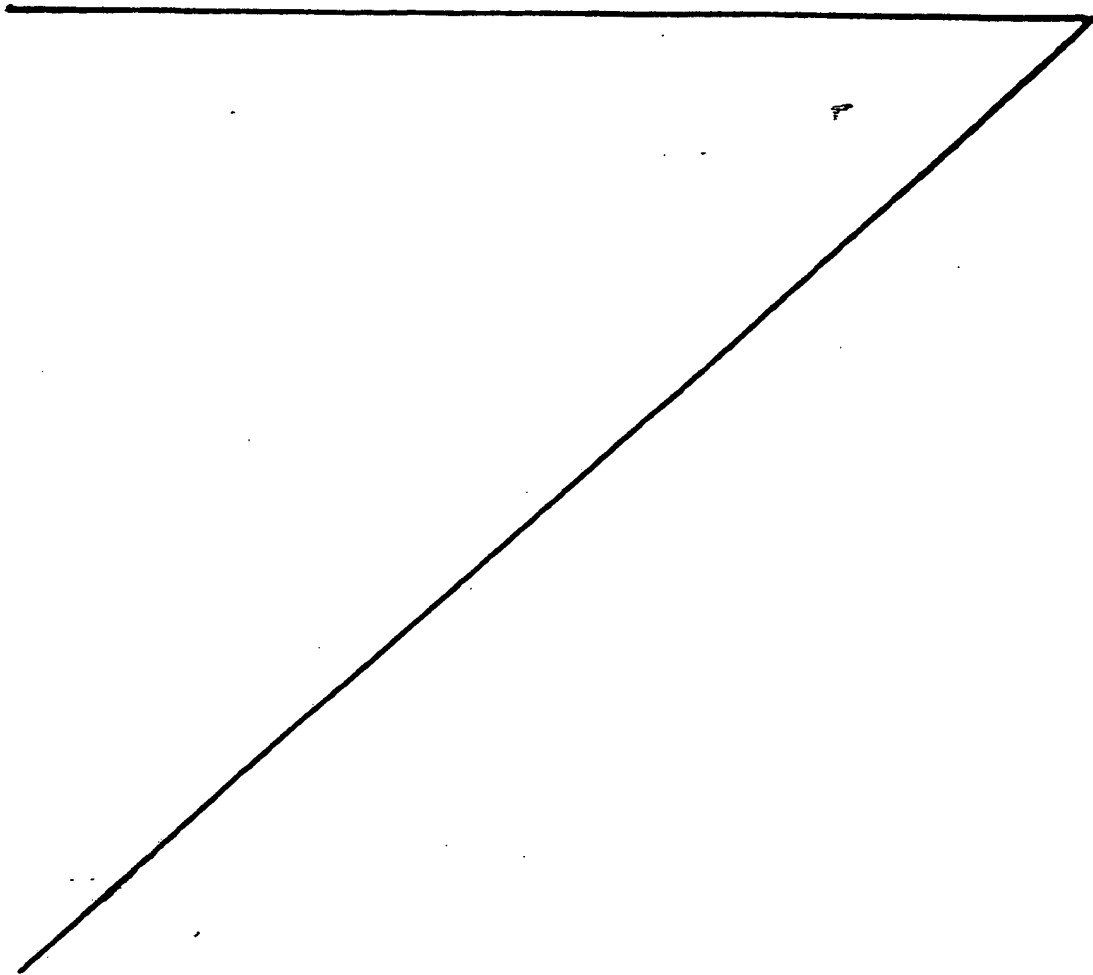
Isopropanol	45.6 parts
Hexane	23.9 parts
VM&P Naphtha	21.6 parts
Macromelt 6900™	8.3 parts
Uvinul D 50	0.332 parts
4-phenylazophenol	0.332 parts

A film 5 to 7 mils thick was cast on a clear mylar backing sheet. Upon drying, the film had average thickness of 0.3-0.5 mils. The modified slip film was then laminated onto a KOR plate which was about 67 mils thick. Laser ablation and imaging was carried out as in Example 6. Once again, the image quality was excellent for all fluences.

Example 8

The printing plates of Examples 6 and 7 were tested for print quality on glossy paper using blue aqueous ink. The ink laydown was good. The letters printed were sharp and undistorted.

5



What is Claimed is:

1           1.    A protective layer for a photocurable article  
comprising  
3               a polymeric matrix and  
              a dopant having a high extinction coefficient in  
5               the range of 300-400 nm, the layer responding to  
              a threshold dosage of radiation at a selected  
7               wavelength by photobleaching of the dopant and  
              photoablation of the polymeric matrix.

1           2.    The layer of Claim 1, wherein the dopant is  
2,2'4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-  
3               dimethoxybenzophenone, 4-phenylazophenol or mixtures  
              thereof.

1           3.    The layer of Claim 1, wherein the selected  
wavelength is 351 nm.

1           4.    A photocurable article comprising  
              a photocurable composition having a low absorbance  
3               of radiation at a selected wavelength in the  
              range of 300-400 nm and further comprising  
5               an initiator activatable at the selected wavelength;  
              a protective layer comprising a polymeric matrix  
7               and a dopant having a high extinction coefficient  
              in the range of 300-400 nm whereby said layer is  
9               photoablated by  
              a threshold exposure to radiation at the selected  
11               wavelength.

*Handwritten notes:*  
- A photocurable + mat.  
- in film or coating  
- UV absorbance  
- and a 4-phenylazophenol

1           5. The photocurable article of Claim <sup>11</sup>4, wherein the  
dopant is 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-  
3       dihydroxy-4,4'-dimethoxybenzophenone or 4-phenylazophenol.

1           6. The photocurable article of Claim <sup>11</sup>4, wherein the  
selected wavelength is 351 nm.

1           7. The photocurable article of Claim <sup>11</sup>4, wherein the  
polymeric matrix is selected from the group comprising  
3       polyacetals, polyacrylics, polyamides, polyimides,  
cellulosic polymers, polybutylenes, polycarbonates,  
5       polyesters, polyethylene, polyphenylene ethers, and  
polyphenylene oxides.

1           8. The photocurable article of Claim <sup>11</sup>4, wherein the  
photocurable composition comprises a photopolymer selected  
3       from the group consisting of polyurethanes, including  
acrylate polyurethanes, acid-modified acrylate  
5       polyurethanes, amine-modified polyurethanes, rubbers,  
including acrylonitrile rubbers, and di- and triblock  
7       copolymers such as those made from styrene-isoprene and  
styrene-butadiene.

1           9. The photocurable article of Claim 8, wherein the  
photocurable composition comprises a photopolymer which is  
3       an amine-modified acrylate polyurethane or styrene-isoprene  
di- or triblock copolymer, or acrylonitrile rubber.

1           10. A method of making a laser imaged printing plate,  
the steps comprising

3           modifying a solid, uncured printing plate with a  
UV absorber;

5           ablating the UV absorber using a laser, thereby  
providing ablated and unablated areas;

7           exposing the printing plate to UV light, thereby  
curing the plate in the ablated areas;

9           developing the plate.

1           11. The method of Claim 10, wherein the UV absorber  
comprises

3           a polymeric matrix and

5           a dopant having a high extinction coefficient in  
the spectral output range of the UV light, the

7           layer responding to a threshold dosage of

radiation at a selected wavelength by

9           photobleaching of the dopant and photoablation of  
the polymeric matrix.

1           12. The method of Claim 11, wherein the dopant is  
2,2'4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-  
3           dimethoxybenzophenone, 4-phenylazophenol or mixtures  
thereof.

1           13. The method of Claim 10, wherein the selected  
wavelength is 350-370 nm.

1           14. The method of Claim 13, wherein the selected  
wavelength is 351 nm.

1           15. The method of Claim 10, wherein the spectral  
output range of the UV light is 300-400 nm.

## **CLAIM AMENDMENTS**

Claims 1-14 (canceled)

Claim 15. (Currently amended) A process for making a photosensitive printing element comprising the steps of:

- providing a photosensitive element comprising:
    - a) a backing layer;
    - b) at least one layer of a photocurable composition on said backing layer;
    - c) at least one ablation layer which is ablatable by laser radiation, wherein the ablation layer is in direct contact with the at least one photocurable layer and has a surface opposite the photocurable layer capable of being exposed to laser ablation, the ablation layer comprising:
      - i) at least one ultraviolet radiation absorbing material;
      - ii) at least one binder which is selected from the group consisting of polyacetals, polyacrylics, polyamides, polyimides, polybutylenes, polycarbonates, polyesters, polyethylenes, polyphenylene ethers, and polyethylene oxides;
- wherein the ablation layer is ablatable from the surface of the photocurable layer upon exposure to laser radiation;
- ablating said ablation layer using a laser, thereby providing ablated and unablated areas forming an image; and
  - flood exposing said ablated element to UV light without a negative, thereby curing said photocurable layer in areas under ablated areas of said ablation layer.

Claim 16. (Canceled)

Claim 17. (Previously presented) The process of claim 15 further comprising developing said exposed element.

Claim 18. (Previously presented) The process of claim 15 wherein said backing layer is transparent.

Claim 19. (Previously presented) The process of claim 15 wherein said photocurable layer includes a polyurethane, acrylonitrile rubber, or a diblock or triblock copolymer made from styrene-isoprene or styrene-butadiene.

Claim 20. (Previously presented) The process of claim 19 wherein said polyurethane is an acid-modified acrylate polyurethane or an amine-modified acrylate polyurethane.

Claim 21. (Canceled)

Claim 22. (Previously presented) The process of claim 15 wherein the at least one binder is a polyamide.

Claims 23-25. (Canceled)

Claim 26. (Previously presented) The process of claim 15 wherein the ultraviolet radiation absorbing material constitutes about 1-20 weight parts per hundred of said ablation layer.

Claim 27. (Previously presented) The process of claim 15 wherein said laser used to ablate said ablation layer emits light having a wavelength of 10.6  $\mu\text{m}$ .

Claim 28-29. (Canceled)

Claim 30. (Previously presented) A process comprising the steps of:



- providing a solid, photocurable printing plate comprising:
  - a backing;
  - at least one layer of a photocurable composition on said backing, said photocurable layer comprising a photopolymer which is unaffected by radiation at a selected wavelength in the range of 300-400 nm and an initiator activatable at the selected wavelength; and;
  - a radiation absorbing layer over said photocurable layer, said radiation absorbing layer comprising a polymeric matrix that is transparent to ultraviolet radiation and a dopant having a high extinction coefficient in the wavelength range of 300-400 nm, wherein said radiation absorbing layer is capable of being photoablated by a laser operating at a first energy level in the wavelength range of 300-400 nm, and wherein unablated areas of said absorbing layer are capable of absorbing at least 95% of irradiated light in the wavelength range of 300-400 nm from an ultra-violet light source operating at a second energy level lower than said first energy level; and
- ablating said absorbing layer using a laser, thereby providing ablated and unablated areas forming an image.

Claim 31. (Previously presented) The process of claim 30 further comprising flood exposing said ablated element to UV light without a negative, thereby curing the photocurable layer in areas under ablated areas of said absorbing layer.

Claim 32. (Previously presented) The process of claim 31 further comprising developing said exposed element.

Claim 33. (Previously presented) The process of claim 30 wherein said backing layer is transparent.

Claim 34. (Previously presented) The process of claim 30 wherein said photocurable

layer includes a polyurethane, acrylonitrile rubber, or a diblock or triblock copolymer made from styrene-isoprene or styrene-butadiene.

Claim 35. (Previously presented) The process of claim 34 wherein said polyurethane is an acid-modified acrylate polyurethane or an amine-modified acrylate polyurethane.

Claim 36. (Previously presented) The process of claim 30 wherein said polymeric matrix includes a polyacetal, polyacrylic, polyamide, polyimide, polybutylene, polycarbonate, polyester, polyethylene, cellulosic polymer, polyphenylene ether, or polyethylene oxide.

Claim 37. (Previously presented) The process of claim 36 wherein said polymeric matrix includes a polyamide.

Claim 38. (Previously presented) The process of claim 36 wherein said polymeric matrix includes a cellulosic polymer.

Claim 39. (Previously presented) The process of claim 38 wherein the cellulosic polymer is hydroxypropylcellulose.

Claims 40-41. (Canceled)

Claim 42. (Previously presented) The process of claim 30 wherein said dopant constitutes about 1-20 weight parts per hundred of said radiation absorbing layer.

Claim 43. (Canceled)

Claim 44. (Previously presented) The process of claim 30 wherein said laser used to ablate said ablation layer emits light having a wavelength of 10.6  $\mu\text{m}$ .

Claim 45. (Previously presented) The process of claim 30 wherein said laser used to ablate said ablation layer emits light having a wavelength of 300-400 nm.

Claim 46. (Previously presented) A process for preparing a flexographic printing plate comprising the steps of:

- providing a solid, photocurable printing plate comprising:
  - a backing;
  - at least one layer of a photocurable composition on said backing, said photocurable layer comprising a photopolymer which is unaffected by radiation at a selected wavelength and power and an initiator activatable at the selected wavelength; and;
  - a radiation absorbing layer over said photocurable layer, said absorbing layer comprising a polymeric matrix that is transparent to ultraviolet radiation and a dopant having a high extinction coefficient in the wavelength range of 300-400 nm, wherein said radiation absorbing layer is capable of being photoablated by a laser at a selected wavelength and power; and
- ablating said absorbing layer using a laser at the selected wavelength and power, thereby providing ablated and unablated areas forming an image.

Claim 47. (Previously presented) The process of claim 46 further comprising flood exposing said ablated element to UV light without a negative, thereby curing the photocurable layer in areas under ablated areas of said absorbing layer.

Claim 48. (Previously presented) The process of claim 47 further comprising developing said exposed element.

Claim 49. (Previously presented) The process of claim 46 wherein said dopant constitutes about 1-20 weight parts per hundred of said radiation absorbing layer.

Claim 50. (Previously presented) The process of claim 46 wherein said laser used to ablate said ablation layer emits light having a wavelength of 10.6  $\mu\text{m}$ .

Claim 51. (Previously presented) The process of claim 30 wherein said laser used to ablate said ablation layer emits light having a wavelength of 300-400 nm.

Claim 52. (Previously presented) The process of claim 15 wherein the ultraviolet radiation absorbing material is selected from the group consisting of benzophenone derivatives and strongly absorbing dyes.

(Lead Suggestion) Skip flr with T.C. U.V. Blocky  
subject is a possible way to make a directly  
large plot. Meeting this idea to J. Rastetter  
+ E. Murphy.

Discuss the laser image feasibility with W. Oton

1. Use U.V. Absorber (MX40 BASF, water ZPA soluble) in slip film to form a U.V. Mask to Fluor Shat Polymer (U.V. curable)
2. Use laser image technology (Thermal Japan) for gravure, to etch & sublimate the slip film to make a ~~image~~ <sup>black</sup> layer on surface
3. Expose the image to U.V. light for photo plot. A ~~disclosure~~ <sup>disclosure</sup> will be filed.

The U.V. absorb or black layer can be resin metal plating or etching

Solubility study of UV absorber in slip film solvent

120 g ZPA  
63 g Hexane  
57 g Naphthalene  
5 g of each the  
MS

AST MS 40 0.1g ✓ 0.2g ✓ + No solubility in the  
DS 49 0.15 x Total solubility

Diphthaloyl ether dimethyl benzoylbenzene x

- ① slip film solvent 20g 0.1g MS 40  
② slip film 10g 0.2g MS 40 + 0.1g carbon black  
did not change  
to much on color

UV Intensity 1.5 mW/cm<sup>2</sup>  
angle 45° 1.2 mW/cm<sup>2</sup>

# 1. Slip film 0.7 mW/cm<sup>2</sup>  
0.6 mW/cm<sup>2</sup>  
2 layers 0.35 mW/cm<sup>2</sup>

# 2 0.45 mW/cm<sup>2</sup>

# 3 0.1g MS 40, 10g slip film 0.1g vicar  
0.5 mW/cm<sup>2</sup>

Try increase film thickness + conc. of MS 40 + carbon black might be  
better

Large Tangle the ship film / polyester on EPIC  
+ 3M. yellow ring proof by YAG 523 623 44  
623 do not have any effect  
YAG & 523 44 have higher than ship 1 Rubber

Ask Terry Juley re do on yellow film to  
see the laser can remove the UV blocky  
Rough 1" square, The 1" YAG still the transmission  
0.1 mW/cm yellow film itself has 0.15 mW/cm  
while using the yellow coating has 16 mW/cm  
but laser effect part only has 9 mW/cm it  
much less transparent

Blender 28883 for PCE Lot # BB 8341  
in pellet form

Blender 28883 in bag Pellet  
Lot 8319 (Cca) ~~pellet~~ form (polybly form)  
8332 (Karton power of sand size form  
pouch  
opaque

Twillison did not have any retain of Lot BB 8341  
he asked sample  
5



Visiting Laser Fare Inc. Springfield R.I.  
with J. Quirk

Mention to Terry Farley. YAK did not attack the  
rubber or sily film layer. The idea is to destroy  
the U.V. checker & dye in sily film layer to ~~create~~  
~~the~~ convert the sily film to a photo tool on  
the plate.

He mention the YAK is 10.2 W. But CO<sub>2</sub>  
is 10.2 W.

By control the intensity YAK might choose the  
plate. CO<sub>2</sub> might burn the plate. If CO<sub>2</sub> laser  
only burn the surface it will work.

Use CO<sub>2</sub> laser to burn sily film on ~~coat~~  
position Mylar. It works partially.  
Try again on EPL 107 plate  
(1" x 1")

Test 1 intensity same as Test 2 (1" x 1")

Test 3 (1" x 1") weaker. Test 4 double

beam of Test 2. (1" x 1")

Test 5 (4.2 W)

# 1, 2. remove 0.1 - 0.2 mil

# 3 remove 0.1 mil

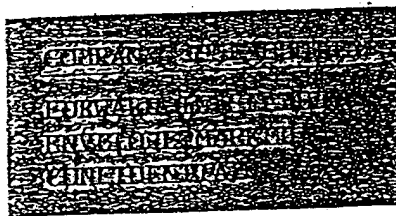
# 4 remove 0.3 mil

# 5 remove 3 mil (No image contrast)  
layer any more)

This test shows the feasibility to use laser to make  
photo tool directly on photo emulsion printing plate

**CONFIDENTIAL AND PRIVILEGED INFORMATION**

To: PATENT DEPARTMENT  
W.R. GRACE & CO.-CONN.  
Grace Specialty Chemicals  
Lexington, MA 02173



Disclosure No. \_\_\_\_\_  
(leave blank)

Fr: EM&S- Printing Product  
Grace Unit or Division

Re: DISCLOSURE OF INVENTION

\*\*\*\*\*

A. TITLE OF INVENTION No Negative Photo Curable Polymer Plate Through  
(brief but descriptive) Laser Ablation.

B. INVENTOR(S)

TYPE/PRINT FULL NAME	CITIZENSHIP	GRACE UNIT
Michael W. Yang	U.S.A.	EM&S
Rustom S. Kanga	India	WRC
_____	_____	_____
_____	_____	_____

(Additional inventors are listed on other side)

C. My/Our invention was conceived (first thought of) on \_\_\_\_\_, 19 \_\_\_\_.

D. My/Our invention was first disclosed on \_\_\_\_\_, 19 \_\_\_\_.  
John Rastetter  
to: Edward Murphy of Printing Prod. orally [x] in writing [ ] (attach copies).

E. The following details and the earliest date are specified as to whether the invention may have been:

- 1) Publicly disclosed as by oral presentation or written publication (Identify audience/recipients if possible by organization and title);  
-- The idea was written in Grace notebook on \_\_\_\_\_, No. 4027, page 71.  
-- On \_\_\_\_\_ meeting with Mr. Terry Feeley, Laser Fare, Inc. in Atlanta, Georgia.

- 2) Sold, offered for sale, or used in commercial production (including any preparatory activity); or

- 3) Sampled, field tested, or evaluated by third parties outside Grace.  
All secrecy agreements in connection with any of the above are noted.

F. Future sampling, testing, evaluation, sale, commercial activity, disclosure, or publication is XX / is not \_\_\_\_\_ planned. (If planned, give earliest anticipated date and details).

- G. **RELATED CASES.** Disclosures, patent searches, or cases now on file or contemplated that closely relate to my/our invention are identified as follows:

See Attachment.

- H. **RELEVANT ART.** Products, processes, compositions, or machines etc. similar to my/our invention and (1) used commercially by others or (2) described in the literature (i.e. advertising, patents, specifications, or other publications) are identified (e.g., as by first dates of usage or publication) as follows:

See Attachment.

- I. **SUMMARY OF INVENTION.** Objectives, key elements, novel features, and differences from and advantages over the relevant art (e.g., problems solved) are briefly set forth in a few lines (detail is provided in para. K) as follows:

Photo tool is an essential element to make a photo curable printing plate. Usually a polyester film with Silver Halide deposition is used to make the photo tool, but it is a costly and an environmental concern process. By adding U.V. block reagent in the protection film layer of photo curable plate, it can turn the protection film to a built-in photo tool by laser ablation.

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- J. **RECORDS.** Notebooks, reports, and other documents which substantiate dates on which the invention was conceived are identified as follows (and copies may be attached):

Grace Notebooks 4027, page 71

and Notebook 17021.

- K. **DETAILED DESCRIPTION OF INVENTION**

Sufficiently detailed particulars are herein described (e.g., permissive and preferred operating ranges, temperatures, concentrations, proportions, etc.) to enable those of ordinary skill in the art to duplicate the invention without further experimentation.

Simplified drawings, diagrams, or flow charts (in ink) are provided below where possible. Critical temperatures, concentrations, proportions, or pressures are noted and substantiated where possible by data. Any additional sheets are signed and dated.

A protection film with composition of:

Macromelt 6900	22.75 g
VMP Naphtha	57 g
IPA	120 g
Hexane	62 g
BASF Uvinul D 50	2 g

Coated on ICI Melinex Type O by Doctor Blade, the thickness of the film is 0.3 mil. The protection film and cover sheet (Melinex Type O) was laminated on Flex-Light KOR plate. During the plate image stage, the plate was back exposed first, then peel off the Melinex Type O cover sheet and leave the U.V. blocking protection film on the surface of KOR plate. A CO<sub>2</sub> laser gun with digital image program was used to ablate the protection film to produce a photo tool on the KOR surface. The ablated KOR plate can be imaged in U.V. exposure unit without using negative and get a great image quality plate.

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In consideration for my/our employment and in accordance with the terms of my/our employment, I/we hereby offer and assign to my/our employer (W.R. Grace & Co.-Conn. or employer-subsidary) to the extent permitted by the national laws which apply to me/us as inventor(s), any and all my/our United States and world-wide rights to the invention described hereinabove and entitled

No Negative Photo Curable Polymer Plate Through Laser Ablation

(TITLE OF INVENTION -should be same as in Paragraph A)

I/we authorize said employer or its successor or assignee to apply for patents in any country in its name or in my/our names as deemed necessary and agree to execute all papers necessary for such patent applications.

[Signature]  
Inventor Signature      Date

Rustum S. Kangra  
Inventor Signature      Date

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